Vibrational spectrum of amorphous silicon: Experiment and computer simulation

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The dynamical structure factor $S(Q,\omega)$ and the vibrational density of states $g(\omega)$ for amorphous silicon have been measured by neutron scattering methods. Computer simulations of $S(Q,\omega)$, based on a 216-atom structural model, are in substantial agreement with experiment.

Insofar as they can be regarded as tetrahedrally bonded continuous random networks, amorphous silicon (*a*-Si) and amorphous germanium are arguably the simplest of amorphous solids. As such, their vibrational properties are of interest for comparing the nature of excitations in amorphous and crystalline solids. Here we present neutron scattering measurements of the wave vector and energy dependence of the vibrational spectrum of *a*-Si and compare these with realistic computer simulations.

The vibrational properties of crystalline solids are understood at a very detailed level in terms of phonons. Comparable understanding does not exist for amorphous solids, although one can anticipate some of the qualitative similarities and differences. At the very least, one expects a smearing of the vibrational spectrum in Q space for a disordered solid, following the idea that its diffuse elastic diffraction pattern is a smeared version of the sharp-line diffraction pattern of the polycrystalline counterpart. A model which incorporates this minimal expectation is the "diffuse-umklapp scattering" picture of Froböse and Jäckle,[1] Hafner,[2] and others. Such a picture notably does not include the two-level states (TLS) which are a feature of most amorphous solids. Tunneling excitations among the TLS have not been observed to date by neutron scattering, and it is to be expected that their detection would be difficult, because of their low energies (in the range of 0.01–0.1 meV) and relatively low density. However, at somewhat higher energies, in the few-meV range for a material such as SiO_2, extra modes have been observed[3] which originate from the same asymmetric double-well potential minima which gives rise to the TLS. Whether extra vibrational modes are to be found in all amorphous solids is unclear and a point which is addressed in the investigations reported here.

The sample used in this and in previous experiments[4] was prepared by rf sputtering in an Ar atmosphere. The deposition rate was ~ 2 μm/h, and several different runs were needed to accumulate the 5-g sample. The Al foil substrates were dissolved off with acid, and the resultant *a*-Si flakes were dried at 100 °C for ~ 12 h to remove adsorbed water. The neutron scattering measurements were mainly carried out on the IN4 time-of-flight spectrometer at the Institut Laue-Langevin, Grenoble, France. Considerations of resolution and intensity dictated the choice of an incident neutron energy E_0 of 12 meV, although a higher E_0 would have been preferable to extend the Q range of the results. Additional data were obtained on a triple-axis spectrometer at Oak Ridge National Laboratory.

The starting point of the computer simulations was the 216-atom network of Wooten *et al.*[5] We assume that *a*-Si can be regarded for our purposes as a crystal with a large unit cell, with a simple potential of the Keating type,[5] yielding 648 zone-center modes with frequencies ω_i and eigenvectors $\mathbf{e}_{ij}$. For comparison with the neutron experiment, one can then calculate[6] the reduced structure factor

$$F(Q,\omega)=\left\langle \left| \sum_j \hat{\mathbf{Q}}\cdot\mathbf{e}_{ij}\exp(i\mathbf{Q}\cdot\mathbf{R}_j) \right|^2 \right\rangle ,$$

where the angular brackets denote averages over all modes i with the same ω, and over all orientations of $\mathbf{Q}$. Each curve in Fig. 1 represents an average over five modes with nearly the same ω. The structure factors for the modes within each group resembled each other to a surprising degree, suggesting that the distinctly different phonon eigenvectors that one can have for modes of the same frequency in a crystalline solid have no amorphous counterpart, i.e., all modes with the same ω in an amorphous solid tend to have similar patterns of vibration as-

sociated with them. States near the band edge ($E \geq 65$ meV) are localized in character, but have very similar structure factors to delocalized states of slightly lower energy (60 meV), implying that it is difficult to address the question of localization by means of neutron scattering measurements.

We compare simulation and experiment primarily in terms of constant-ω cuts of the scattering law

$$S(Q,\omega)=(\hbar Q^2/2m)e^{-2W}[2\omega \sinh(\beta\omega)]^{-1}F(Q,\omega) ,$$

which, apart from trivial factors, is the reduced structure factor multiplied by Q^2 times the Debye-Waller factor e^{-2W}. Thus the comparison between theory and experiment in Fig. 2 is essentially that of the orientationally-averaged Fourier transform of the pattern of vibration, averaged over modes with the same ω. The solid lines in Fig. 2 are simply smooth curves drawn through the points of Fig. 1, multiplied by Q^2e^{-2W}, with the vertical scale for each calculated curve adjusted to best fit the experimental data. The frequencies chosen for the comparisons in Fig. 2 are indicated by arrows on the top part of Fig. 3, in which are shown densities of states $g(\omega)$ derived from the neutron scattering experiment and from the computer simulation. The experimental $g(\omega)$ for a-Si is very similar to that reported in a previous paper,[4] but is more reliable and accurate. We have also measured[7] $g(\omega)$ for a-Ge (not shown), which is very similar in shape to that of a-Si, but with the significant difference that there is no indication in a-Ge of extra low-energy modes, a point we shall discuss later. Maley, Lannin, and Price[8] (MLP) have recently reported similar measurements of $g(\omega)$ for a-Ge. Their data are in good agreement with our own, considering differences in methods of data acquisition and analysis. Their comparisons of $S(Q,\omega)$ with theory were restricted to a simple analytic model involving only nearest-neighbor correlations, showing some large deviations at low Q. The longer-range correlations that MLP recognized needed to improve agreement in this Q range are of course included in the detailed computer simulation of the present work.

Also shown in Fig. 3 is a $g(\omega)$ measured for polycrystalline Si (pc-Si), obtained under the same experimental conditions employed for a-Si. There is very good agreement with a $g(\omega)$ calculated from a model[9] which accurately fits the phonon dispersion curves of Si. The pc-Si results are useful mainly for directly demonstrating the reliability of the experimental method and techniques of data analysis. The counterparts of the four main peaks in the pc-Si $g(\omega)$, usually labeled TA, LA, LO, and TO, in order of increasing energy, become smeared but are clearly identifiable in the a-Si spectrum. The a-Si $g(\omega)$

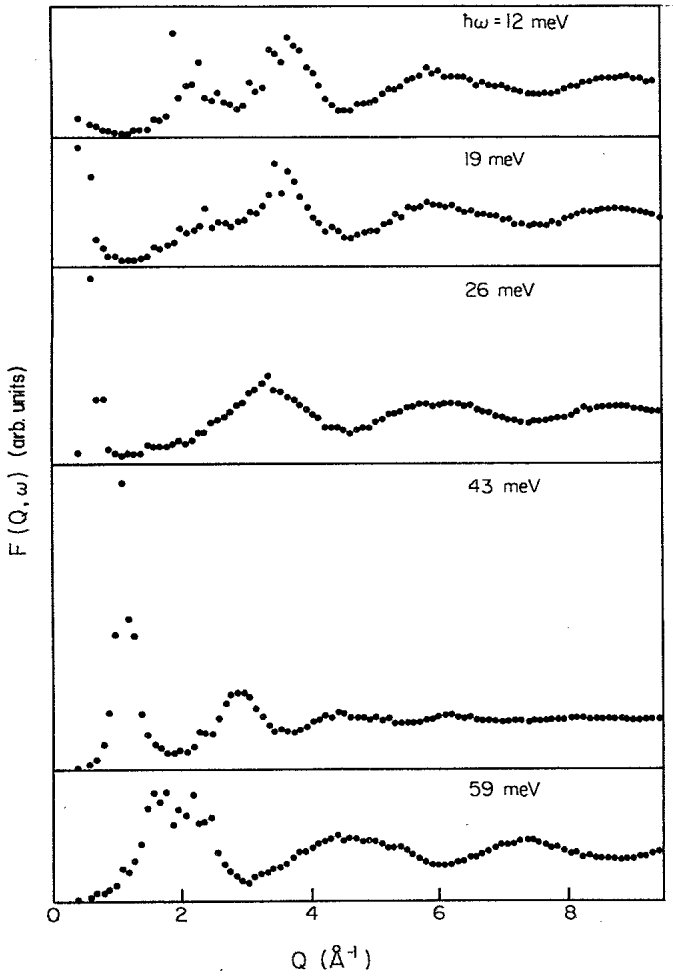

FIG. 1. Reduced structure factors $F(Q,\omega)$ for a-Si, obtained from the computer simulation described in the text.

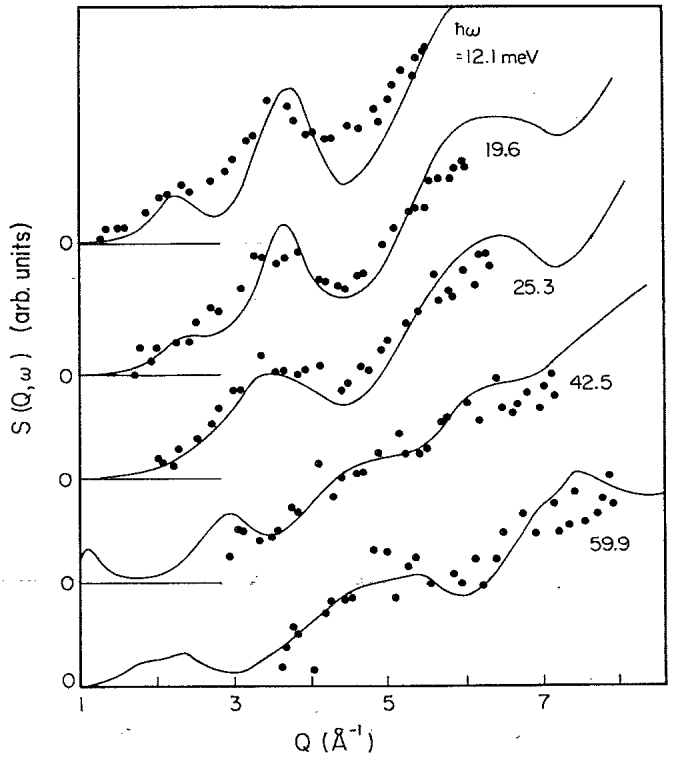

FIG. 2. Constant-ω cuts of $S(Q,\omega)$ for a-Si, obtained by neutron scattering (points) and from the computer simulation (lines).

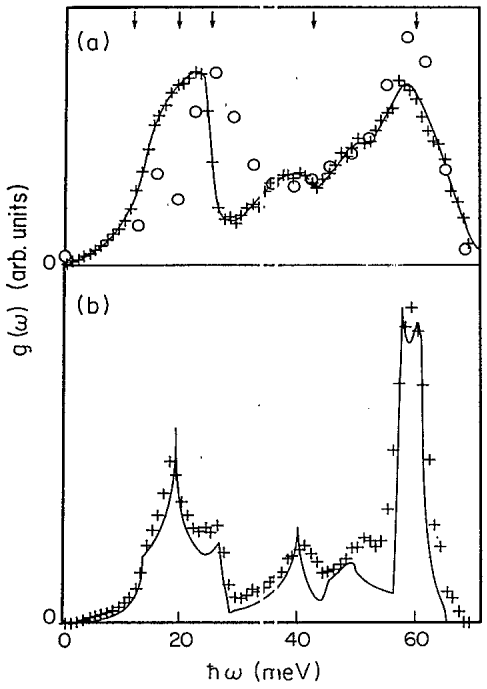

FIG. 3. Experimental and theoretical vibrational densities of states for (a) amorphous and (b) polycrystalline silicon. For both (a) and (b), the experimental results are the crosses, connected by a line to guide the eye in (a). The calculated a-Si spectrum (open circles) was obtained from the computer simulation, while the calculated p-Si spectrum, the solid line in (b), comes from Ref. 9.

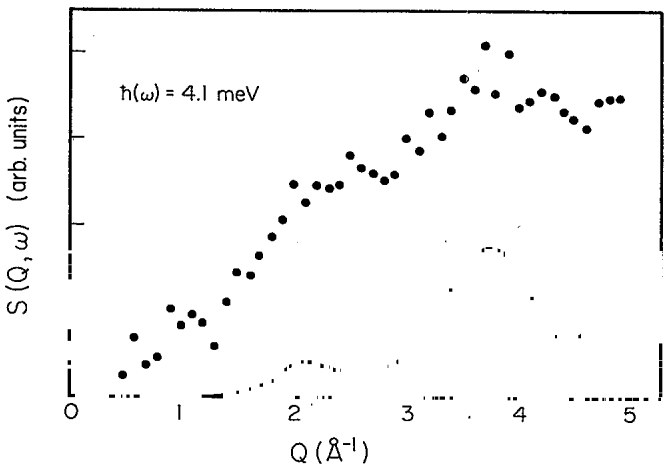

FIG. 4. Constant-ω cut of $S(Q,\omega)$ obtained by neutron scattering (points), compared with the contribution expected (shaded area) from acoustic-phonon-like modes. A substantial contribution from excitations of unknown origin is apparent.

from the computer simulation is in fairly good agreement with experiment, but places the "TA"-like band at too high an energy (26 meV, cf. 20 meV from experiment). This indicates that the bond-bending forces in the Keating model were overestimated here by about 30% but the same parameters are likely to be valid for both amorphous and crystalline silicon. Also, the computed "TO"-like peak at 60 meV is somewhat too sharp, as in previously reported simulations,[10] suggesting that the bond-angle distribution is narrower in the Wooten network[5] than in our a-Si sample.

Returning to the comparison between theoretical and experimental $S(Q,\omega)$ cuts in Fig. 2, the agreement is in general rather good, especially for $\hbar\omega=25.3$, 42.5, and 59.9 meV. For $\hbar\omega=12.1$ and 19.6 meV, the agreement is only fair, the experimental spectra showing less pronounced structure than the calculated ones. We believe that the reason for this difference is that there is an extra contribution to the scattering which is a rather featureless, monotonically increasing function of Q, and that the observed scattering is a sum of the scattering from a continuous random Si network, plus the extra scattering. The Q dependence of the "TA"-like modes ($\hbar\omega=12.1$, 19.6, 25.3 meV) mirrors $S(Q)$, the elastic structure factor,[11] corresponding to "in-phase" motions of the atoms with surrounding atoms. For the "TO"-like 59 meV modes, the motions are "antiphase," leading to peaks in $S(Q,\omega)$ where $S(Q)$ has valleys, and vice versa. For $\hbar\omega=42$ meV, neither in-phase nor antiphase is an accurate description, leading to a somewhat smoother Q dependence.

The existence of extra scattering at low energies is more clearly demonstrated by a cut of $S(Q,\omega)$ at constant $\hbar\omega=4.14$ meV, similar to the data of Fig. 2, but obtained on a triple-axis spectrometer in a manner such that the proportion of the scattering which is expected from phononlike excitations, the shaded portion in Fig. 4, can be easily and reliably estimated. The estimate derives from the "diffuse umklapp scattering" picture,[1,2] and shows that acoustic-phonon-like excitations account for less than half of the scattering at 4.14 meV, implying the existence of a high density of extra excitations of unknown origin at this energy. Although it is tempting to claim that the extra excitations are intrinsic to a continuous random network and to the amorphous state of condensed matter, we believe that this is not the case, and that they in fact arise from extraneous sources, e.g., surface modes associated with microvoids occluded during film deposition. Preliminary calculations on a-Si models[12] with greater concentrations of defects show that the vibrational density of states is quite insensitive to fine details of the microstructure. Our point of view is consistent with other evidence[13] that extra vibrational modes and TLS are absent for "ideal," i.e., continuous-random-network, a-Si or a-Ge.

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